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(54) **A process for the direct or indirect electro-deposition of a highly corrosion resisting crack-free technical hard chromium plating layer**

(57) A process for the direct or indirect deposition of a highly corrosion resisting technical hard chromium plating layer on the surface of a metallic workpiece from an aqueous working electrolyte containing chromic acid and sulphate ions is described. In a process wherein the current yield of the working electrolyte is optimised by the addition of at least one saturated aliphatic sulphonic acid having at the most two carbon atoms and at the most six sulphonic acid groups and or by the addition of salts or halogen derivatives thereof and the deposit has a thickness of at least 2μm and a hardness exceeding 9øø HV ø.1, the deposition is effected with direct current pulses, the pulse frequency lying in the range between a lower critical pulse frequency dependent on the cathode current density setting and an upper critical pulse frequency point dependent on the optimised current yield at the same current density. The procedures for determining the lower critical pulse frequency and the upper critical pulse frequency point are described. The on-off ratio in the range between the lower critical pulse frequency and the upper critical pulse frequency point is kept sufficiently low for the deposit to remain bright and substantially crack-free.

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Fig.1

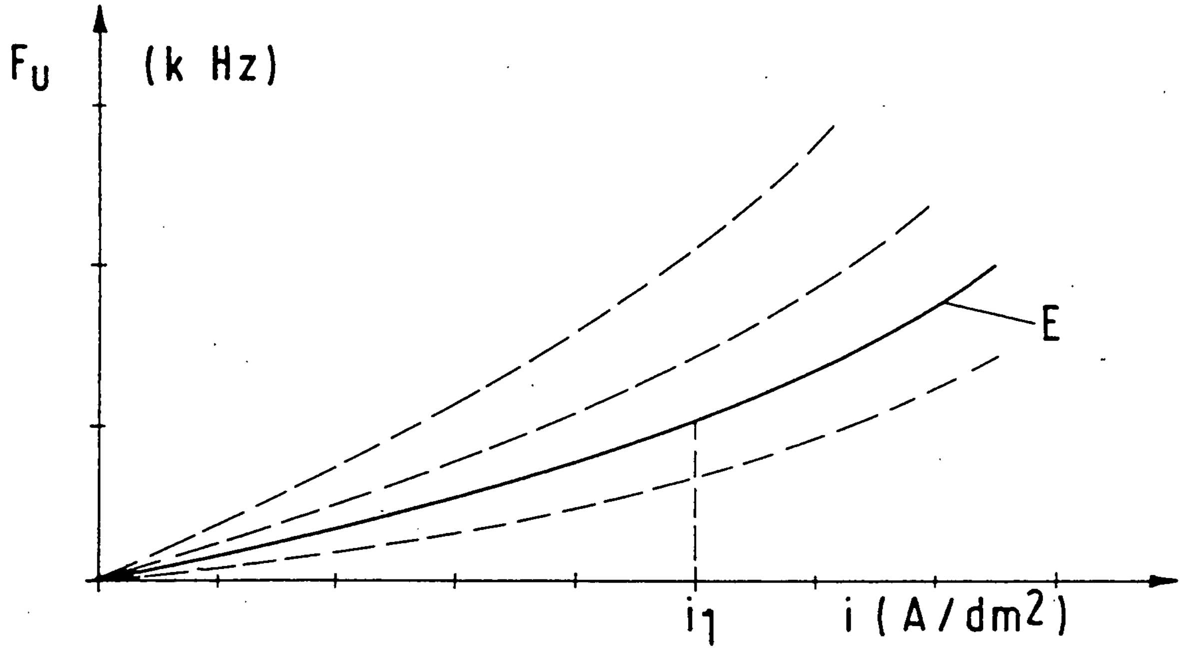
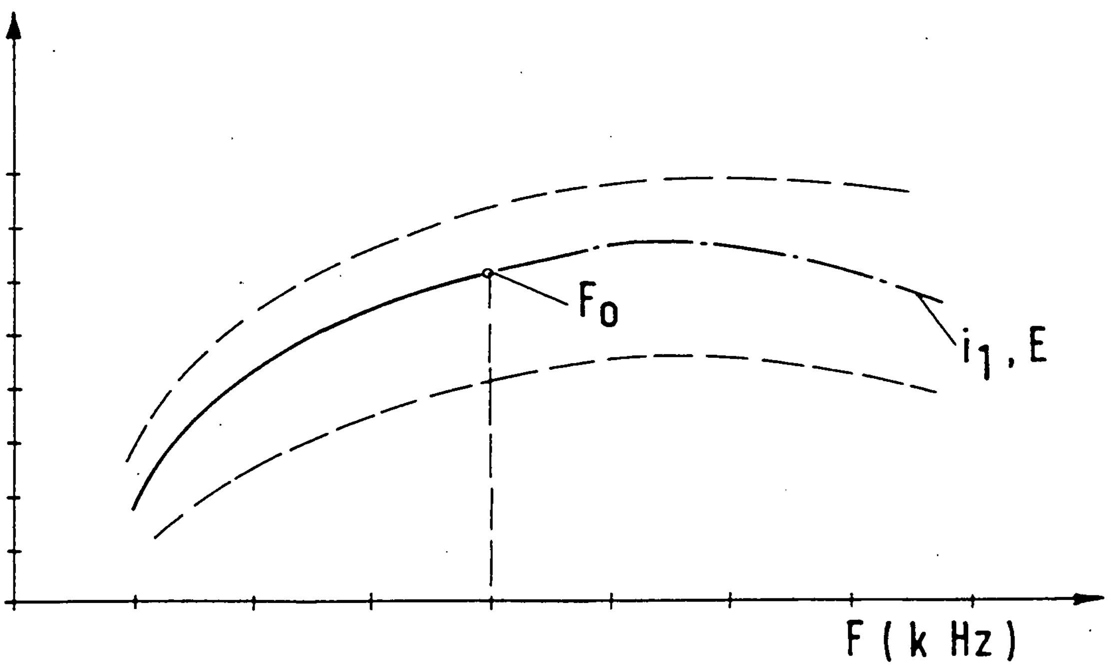



Fig.2



# Fig.3

| TABLE | PULSE FREQUENCY in Hz | ON-OFF RATIO E in % | MEAN CATHODE CURRENT DENSITY in A/dm² | CATHODE CURRENT YIELD in % | APPEARANCE | HARDNESS in HV 0,1 | CRACKING STATE | SALT SPRAY TEST. LIFE, h DIN 50 021-SS ASTM B 117-73 ISO 3768-1976 |
|---|---|---|---|---|---|---|---|---|
| | 250 | 50 | 50 | 18,8 | matt | < 900 | CRACKED | < 100 h |
| | 500 | 50 | 50 | 19,5 | matt | < 900 | CRACKED | < 100 h |
| | 1000 | 50 | 50 | 13,6 | matt/BRIGHT | | TRANSITION RANGE | $(F_U)$ |
| 1 | 2000 | 50 | 50 | 18,7 | BRIGHT | >900 | CRACK FREE | >1000 h |
| | 3000 | 50 | 50 | 20,9 | BRIGHT | > 900 | CRACK FREE | >1000 h |
| | 4000 | 50 | 50 | 22,6 | BRIGHT | >900 | TRANSITION RANGE | $(F_O)$ |
| | 5000 | 50 | 50 | 23,7 | BRIGHT | >900 | CRACKED | <100 h |
| | 1000 | 80 | 50 | 22,6 | BRIGHT | >900 | CRACKED | <100 h |
| | 2000 | 80 | 50 | 24,1 | BRIGHT | >900 | CRACKED | <100 h |
| 2 | 3000 | 80 | 50 | 25,4 | BRIGHT | >900 | CRACKED | <100 h |
| | 4000 | 80 | 50 | 25,8 | BRIGHT | >900 | CRACKED | <100 h |
| | 5000 | 80 | 50 | 26,3 | BRIGHT | >900 | CRACKED | <100 h |

# A PROCESS FOR THE DIRECT OR INDIRECT DEPOSITION OF A HIGHLY CORROSION RESISTING TECHNICAL HARD CHROMIUM PLATING LAYER

This invention relates to a process for the direct or indirect deposition of a highly corrosion resisting technical hard chromium plating layer on the surface of a metallic workpiece from an aqueous working electrolyte containing chromic acid and sulphate ions at a constant cathode current density, the current yield being optimised by the addition of at least one saturated aliphatic sulphonic acid having at the most two carbon atoms and at the most six sulphonic acid groups and/or by the addition of salts or halogen derivatives thereof, and the hard chromium layer having a thickness of at least 2 µm and a minimum hardness of 900 HV 0.1 in conformity with DIN ISO 4516. The sulphonic acid can also be formed within the electrolyte by chemical or electrochemical reactions between appropriate raw materials. The workpieces in question are primarily steel, aluminium or copper products. In the matter of current yield optimisation by the additives quoted, reference is made to DE 34 02 554. The current yield denotes the ratio between the actual and theoretical amounts of metal deposited on the cathode. It can be optimised in the process of the above mentioned basic nature by adjusting the amounts of additives provided. The working electrolyte can obviously be further modified to adapt it to different chromium plating applications and working conditions, by the inclusion of known additives for other purposes or formulation with fluoride ion or fluorine complex additives. On the other hand, it must always remain feasible to optimise the

current yield as described above, though the optimisation effect can be less pronounced if fluorine compounds are added than in the case of electrolytes without fluorine compounds. In the context of the invention, it is preferred to use a working electrolyte free from fluorine compounds. Technical hard chromium plating is used for chromium finishes with technical functions on metallic workpieces, notably in steel or aluminium alloy. It is usually deposited directly on the parent material. However, the parent material can first be plated with underlayers of copper, copper alloys, nickel, zinc, zinc alloys or nickel alloys with phosphorus or boron deposited non-electrolytically. Furthermore, technical hard chromium platings differ in respect of normal layer thicknesses from decorative bright chromium platings, which are used in a layer thickness range between merely 0.2 and 2 µm. Hard chromium layers are thicker. The practical range for technical hard chromium plate commences at 2 µm, and the range is often between 5 and 100 µm. Such layers are intended as protection against wear and corrosion. In certain cases, technical hard chromium platings can be applied in thickness extending into the millimetres range. Thus, worn components can be as it were built up with hard chromium plating.

In the known process on which the invention is based (DE 34 02 554), plating is carried out with direct current. Direct current can be used to deposit bright hard chromium coatings from working electrolytes of the basic type initially described or modified as indicated. Care is often taken to

limit the residual undulation of the direct current to below 5%, since excessive residual undulation can give rise to more or less matt deposits of seriously reduced hardness. The hard chromium layers deposited by the known process contain closely arrayed fine cracks, i.e., micro-cracks. Their corrosion resistance is satisfactory but could be further enhanced.

The object of the invention is to provide a process as initially described under conditions whereby the corrosion resistance of the hard chromium layer is further enhanced, but the current yield remains at the maximum attainable level.

According to the present invention, there is provided a process for the direct or indirect deposition of a highly corrosion resisting technical hard chromium plating layer on the surface of a metallic workpiece from an aqueous working electrolyte containing chromic acid and sulphate ions at a constant cathode current density, the current yield being optimised by the addition of at least one saturated aliphatic sulphonic acid having at the most two carbon atoms and at the most six sulphonic acid groups and/or by the addition of salts or halogen derivatives thereof, and the hard chromium layer having a thickness of at least 2 µm and a minimum hardness of 900 HV 0.1 in conformity with DIN ISO 4516, the deposition being effected with direct current pulses, the pulse frequency lying in the range between

a lower critical pulse frequency ($F_U$) dependent on the cathode current density setting and an upper critical pulse frequency point ($F_O$) dependent on the optimised

current yield at the same current density,

the lower critical pulse frequency ($F_U$) for the working electrolyte being determined by measuring and constructing a curve of pulse frequencies against current densities below which the hardness of the deposit is below the minimum hardness, whilst above it the deposit is bright and free from cracks and has a hardness above the minimum hardness, and the upper critical pulse frequency point ($F_O$) for the working electrolyte being determined by measuring and constructing a curve of current yields against pulse frequencies, at the same current density giving the optimised current yield and extending up to the upper critical pulse frequency point ($F_O$) beyond which the bright crack-free deposit changes into increasingly cracked deposits with increasing pulse frequencies, the on-off ratio of the direct current pulses in the range between the lower critical pulse frequency ($F_U$) and the upper critical pulse frequency point ($F_O$) being kept sufficiently low for the deposit to remain bright and substantially crack-free.

Below the curve of pulse frequencies against current densities, the deposit is substantially useless as hard chromium plating since its hardness is too low. It generally appears matt and is rougher than bright deposits. Moreover, it is often cracked or micro-cracked. The on-off ratio is defined as the sum of the pulse periods divided by the total processing period spent by the workpiece in the electrolyte. It is specified as a percentage. Substantially crack-free denotes that the number of cracks is infinitesimally small

compared to those in the known bright hard chromium deposits, and that the cracks no longer significantly influence the corrosion behaviour of the deposit. In a preferred embodiment of the invention within the scope of the basic teaching just specified, the cathode current density is set within the range of 10 to 1200 A/dm$^2$ uually adopted in the known direct current process, but under the invention it is defined as the arithmetic mean of the current densities over each direct current pulse cycle. In the process of the invention, the cathode current yield is mostly in the 10 to 25% range. It is possible under the invention to produce laminated hard chromium deposits, more particularly by first depositing a crack-free hard chromium layer and then, without interruption and using the same working electrolyte, depositing a bright but cracked hard chromium layer. In order to deposit the second finely- to micro-cracked layer, one only needs to abandon the basic teaching just specified and operate outside the resulting range between the lower critical pulse frequency point $F_U$ and the upper critical pulse frequency point $F_O$. In order to effect this, and furthermore in order to construct the curves of pulse frequencies against current densities and current yields against pulse frequencies, the invention recommends the use of a current source with which the current density, the pulse frequency and the on-off ratio are variable. It is obviously possible under the invention to use the widest variety of pulse forms.

It is known in principle to deposit hard chromium with direct current pulses (cf.T.Pearson and J.D.Dennis, "Effect of

pulsed current on the properties of electrodeposited chromium", contributed to the 12th World Congress of Surface Finishing, 4 to 7 October, 1988, Paris). In this case, more or less bright and substantially crack-free deposits were obtained. However, in this known case very low pulse frequencies in the range 16 to 500 Hz were used to ensure more or less bright and substantially crack-free deposits, and the reproducibility is uncertain. When teaching of the invention is adopted, the pulse frequency is mostly in the 500 to 5000 Hz range. The on-off ratio is mostly in the 30 to 70% range.

The accruing advantages are to be seen in that under the invention one can reproducibly deposit hard chromium layers as initially defined, which are bright and substantially crack-free at the usual hard chromium plating thicknesses and at the same time are deposited at relatively high cathode current yields. It is particularly advantageous that one can additionally deposit a hard chromium layer constituting a finely- to micro-cracked cover coat of chromium, which is often called for by virtue of its superior friction properties. The network of cracks in this case functions as oil pockets.

It makes no difference to the results if the direct current pulses are modified by integrated anodically acting current pulse components, so long as their pulse frequency is very small and their current densities not excessive.

The invention arises from the discovery that three prior conditions must be met in order to deposit a bright and

substantially crack-free hard chromium layer of high corrosion resistance, from working electrolytes of the basic type initially described, viz:-

a) the pulse frequency must be increased as the cathode current density setting for the chromium plating process is raised;

b) nevertheless, the pulse frequency must not be too high in relation to the optimised current yield;

c) the on-off ratio must be set sufficiently remote from the direct current state.

The invention provides clear criteria for a) and b). The corresponding on-off ratio in conformity with c) can readily be found by trial and error.

The invention will now be described in more detail, with reference to graphs and a typical embodiment. Thus:

Figure 1 is a curve of the critical pulse frequency as a function of the current density;

Figure 2 is a curve of the optimised current yield as a function of the pulse frequency; and

Figure 3 presents Tables 1 and 2 relating to a specific typical embodiment.

Figure 1 qualitatively presents the graph of pulse frequencies against current densities for a specific working electrolyte formulated in accordance with the invention. The pulse frequencies are plotted vertically and the arithmetic mean current densities horizontally. Below the curve, which rises with increasing current densities, hard chromium deposits are formed as matt finishes, cracked or crack-free

but of lower than minimum hardness. Above the curve, the hard chromium deposits are crack-free, bright and of higher than minimum hardness. Consequently, the curve indicates the lower critical pulse frequency $F_U$ as a function of the current density. The on-off ratio E appears on the curve as a parameter. Other on-off ratios produce other curves, as indicated by dashed lines in Figure 1. - If $t_1$ denotes the duration of an ideal square-wave current pulse and $t_2$ the duration of the current pause, the pulse frequency in Hz is given by $F = 1\ (t_1 + t_2)$. The on-off ratio is defined as $E = 100 \cdot t_1\ (t_1 + t_2)$ percent. It is self-evident that the curve of pulse frequencies against current densities can only be recorded up to the point beyond which there is no single-valued correlation between the critical pulse frequency and the current density.

Figure 2 qualitatively presents a curve of current yields against pulse frequencies, relating to the same electrolyte and the current density setting $i_1$ and the same on-off ratio E as indicated on the continuous curve in Figure 1, for a specific deposition requirement, the current yield having already been optimised as described above by adjusting the amounts of additive used, the said additive being made up of at least one saturated aliphatic sulphonic acid having at the most two carbon atoms and at the most six sulphonic acid groups, and or salts or halogen derivatives thereof. The current yields are plotted vertically and the pulse frequencies horizontally. This optimum current yield curve passes through an upper critical pulse frequency point $F_O$.

Beyond the said point $F_O$ the curve has dashes and dots indicating that increasingly cracked deposits will form in this range. Other selected current densities and other on-off ratios lead to different curves. Thus, there arises a family of curves as indicated by dashes in Figure 2.

It is invariably possible to select an on-off ratio, in a range between $F_U$ and $F_O$, such that a bright and substantially crack-free hard chromium deposit of the usual thickness and a higher than minimum hardness is produced. Experience has shown that the range between $F_U$ and $F_O$ can be widened if the thickness of the hard chromium deposit is kept to a minimum. In other words, it is always easier to produce a crack-free deposit if the thickness of the deposit is minimised. In fact, if very low cathode current densities, for example 10 to 20 $A/dm^2$, are used it is even possible to produce very bright and crack-free chromium deposits which are quite acceptable as decorative bright chromium finishes.

Typical Embodiment

An electrolyte for the deposition of a hard chromium layer on the surface of a steel workpiece was formulated as follows;

| | |
|---|---|
| chromic acid as $CrO_3$ | 300 g/l |
| sulphuric acid | 1.3% (of the $CrO_3$ content) |
| ammonium fluorooctane sulphonate | 10 mg/l (as wetting agent) |
| anodes | PbSn5, platinised Ti or platinised Ti-Pd alloy |

When using platinised anodes, an additional 1 g/l of

lead carbonate was provided in the electrolyte. In this connection, direct current deposition in the electrolyte of this composition gave a cathode current yield of 16%. The cathode current yield was optimised as described by the addition of 3.2 g/l of a saturated aliphatic sulphonic acid having a single carbon atom and a single sulphonic acid, which raised it to 27%. In both cases, the cathode current density was 50 A/dm$^2$ and the electrolyte temperature 55°C.

Deposition was next switched to direct current pulse settings and, using various on-off ratios, certain curves of pulse frequencies against current densities were obtained; these will be described later. The detailed procedure was as follows:-

Piston rods of diameter 7 mm, in grade C 45 k material, were finish ground and brushed to a roughness depth Rz less than 1.5 µm, and plated with hard chromium after the cleaning and degreasing stages ordinarily included in electroplating processes. Using a given mean cathode current density and pulses of a given on-off ratio, the critical pulse frequencies $F_U$ were determined at which the deposit changed from having a matt finish and a hardness lower than 900 HV 0.1 to a bright finish with a hardness exceeding 900 HV 0.1, $F_U$ varying with the current density setting. The electrolyte temperature setting was held at 55°C throughout. The thickness of the hard chromium deposits was around 25 µm in every case.

It will be obvious that the transition from matt to bright finishes is gradual, particularly since the actual

local cathode current densities inevitably vary with the workpiece geometry. The critical pulse frequencies $F_U$ represent the midpoints of a transition range. In the experiments, the range producing bright hard chromium deposits was monitored by parallel optical microscope examinations (to distinguish between cracked and crack-free).

Figure 1 schematically shows the resulting family of pulse frequency curves against current densities.

A nominal mean cathode current density setting of 50 $A/dm^2$ was selected for one particular hard chromium plating application, in conformity with the workpiece surface area. According to Figure 1, this corresponds to a lower critical frequency $F_U$ of 1000 Hz, for an on-off ratio of 50%.

Taking this cathode current density setting and the same on-off ratio, a curve was plotted of current yields against pulse frequencies, at least until an upper critical pulse frequency point $F_O$ was reached, at which the hard chromium deposit, though still bright and harder than 900 HV 0.1, reverted to the cracked state. By varying the current density and or the on-off ratio, one can plot a family of current yield curves against pulse frequencies, each terminating at its own critical pulse frequency point.

Figure 2 schematically shows this family of current yield curves against pulse frequencies. In more detail, the procedure for determining this family of curves was as follows:-

Deposits were applied to piston rods, in the same way as for Figure 1, at thicknesses of around 25 µm. The cathode

current yield was determined as a percentage of the theoretical 100% metal recovery at the cathode, by weighing to find the amount of chromium deposited and recording the consumption in ampere-minutes. Everyone versed in the art is familiar with the calculation of Faraday equivalents.

Difficulties can arise in the identification, under an optical microscope, of incipient cracking at the upper pulse frequency point $F_O$. A more reliable verdict was ensured by corrosion resistance testing using the salt spray test (DIN 50 021-SS, ASTM B 117-73 or ISO 3768-1976). In fact, everyone versed in the art is aware that hard chromium plating deposited with direct curent to thicknesses of around 25 μm will only give salt spray test lives shorter than 100 h, if the deposit is bright and cracked or micro-cracked. Hence, if pulse conditions produce substantially longer lives in the salt spray test, the indications are that the deposits in question are substantially crack-free.

Table 1 in Figure 3 relates to the embodiment just described, using a mean cathode current density of 50 A/dm$^2$, an on-off ratio of 50% and an electrolyte temperature of 55°C. It discloses the favourable working pulse frequency range for bright, substantially crack-free and hence highly corrosion resistant hard chromium plating.

Table 1 shows that the same rule applies to every pulse frequency in the range between the lower critical pulse frequency $F_U$ = 1000 Hz and the upper critical pulse frequency $F_O$ = 4000 Hz, viz., that at the quoted current density and within the quoted pulse frequency range it is possible to set

the on-off ratio sufficiently low to ensure that a bright, substantially crack-free and highly corrosion resisting hard chromium deposit of the required hardness is produced.

Table 2 in Figure 3 on the other hand shows that cracked hard chromium deposits with greatly inferior corrosion resistance will be produced if the selected on-off ratio is too high for the pulse frequency range in question. Furthermore, Table 1 also shows that cracked deposits will be produced if the pulse frequency setting lies outside the quoted pulse frequency range.

The experiments were repeated at other current densities such as 40 $A/dm^2$ or 60 $A/dm^2$. The foregoing rule was confirmed. The foregoing rule has also been confirmed in experiments with electrolytes of different compositions.

A already stated, settings with too high an on-off ratio and/or too high a pulse frequency, which produce bright but cracked deposits, can be adopted in order to deposit, preferably without current interruption, to deposit a bright but cracked covering layer on the bright and substantially crack-free underlayer. In other words, double hard chromium finishes with superior friction properties can be produced in this way. If the on-off ratio is set at E = 100%, this means that the cover layer is deposited wih direct current.

Furthermore, the addition of the alkylsulphonic acid used to optimise the cathode current yield exerts a superior brightening action on direct current pulse deposits, provided the working conditions are set above the lower critical pulse frequency $F_U$. A shortage of this additive is reflected in a

loss of lustre in the appearance of the hard chromium deposit over and above the inferior cathode current yield effect.

In connection with the production of double layers as already described, it is within the scope of the invention to automate the measurement and adjustment, at freely selectable rates, of the pulse frequency and/or the on-off ratio of the direct current pulses, with the aid of a freely programmable current- or time-dependent analogues extending to higher pulse frequencies up to or beyond 5000 Hz, and/or higher on-off rates up to 100%, so that as the deposit builds up it becomes cracked instead of crack-free, whilst at the end of the programme the pulse frequency and/or on-off ratio settings are automatically restored to their initial values, preparatory to initiating the next chromium plating cycle.

CLAIMS

1. A process for the direct or indirect deposition of a highly corrosion resisting technical hard chromium plating layer on the surface of a metallic workpiece from an aqueous working electrolyte containing chromic acid and sulphate ions at a constant cathode current density, the current yield being optimised by the addition of at least one saturated aliphatic sulphonic acid having at the most two carbon atoms and at the most six sulphonic acid groups and/or by the addition of salts or halogen derivatives thereof, and the hard chromium layer having a thickness of at least 2 μm and a minimum hardness of 900 HV 0.1 in conformity with DIN ISO 4516, the deposition being effected with direct current pulses, the pulse frequency lying in the range between

a lower critical pulse frequency ($F_U$) dependent on the cathode current density setting and an upper critical pulse frequency point ($F_O$) dependent on the optimised current yield at the same current density,

the lower critical pulse frequency ($F_U$) for the working electrolyte being determined by measuring and constructing a curve of pulse frequencies against current densities below which the hardness of the deposit is below the minimum hardness, whilst above it the deposit is bright and free from cracks and has a hardness above the minimum hardness, and the upper critical pulse frequency point ($F_O$) for the working electrolyte being determined by measuring and constructing a curve of current yields against pulse frequencies, at the same current density giving the optimised current yield and

extending up to the upper critical pulse frequency point ($F_O$) beyond which the bright crack-free deposit changes into increasingly cracked deposits with increasing pulse frequencies, the on-off ratio of the direct current pulses in the range between the lower critical pulse frequency ($F_U$) and the upper critical pulse frequency point ($F_O$) being kept sufficiently low for the deposit to remain bright and substantially crack-free.

2. A process as in Claim 1, wherein the cathode current density is set within the range of 100 to 1200 A/dm$^2$.

3. A process as in Claim 1 or Claim 2, wherein the cathode curent yield lies between 10 and 25%.

4. A process as in any preceding Claim, wherein the pulse frequency is set within the range of 500 to 5000 Hz.

5. A process as in any preceding Claim, wherein the on-off ratio of the direct current pulses is set within the range of 30 to 70%.

6. A process as in any preceding Claim, wherein a crack-free and bright hard chromium layer is first deposited and then, preferably without interruption, a bright but cracked hard chromium layer is deposited thereon.

7. A process as in any preceding Claim, wherein use is made of a current source, the current density, pulse frequency and on-off ratio of which are variable.

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